XXII. *On the Thermal Resistance of Liquids.* *By* Frederick Guthrie. *Communicated by Professor* Tyndall, *LL.D., F.R.S.*

## I. *Introduction.*

§ 1. THE passage of heat through matter has been mainly examined in reference to the diathermancy of solids, liquids, and gases to radiant heat, and to the conduction of contact-heat through solids and gases. The conduction of contact-heat through liquids forms a chapter in heat transference which has not hitherto received as much attention from experimental physicists as it merits.

§ 2. In the following pages I have the honor of submitting to the Royal Society certain experimental results and considerations to which I have been led during an investigation of this subject. These results are necessarily incomplete. The inquiry is fraught with very numerous and considerable experimental difficulties; but I venture to hope that such as the results are, they may be found useful to those who shall hereafter pursue the subject with greater skill and more perfect appliances.

§ 3. It need scarcely be stated that the great majority of the experimental results obtained do not appear in this Memoir. Such results, though of great interest to the experimenter and invaluable for his guidance, have of course been suppressed, having been superseded during the investigation by those obtained through the application of successive improvements to the apparatus employed.

§ 4. I have been induced to pursue this investigation with some perseverance, because I am convinced that it is by means of liquids rather than of solids that we are destined to gain ultimately an exact experimental determination of the conduction of heat in all cases. By their means we shall gather data concerning the conductive indices or thermal resistances of the elements, and be able to determine the effect on such resistance caused by the change of chemical nature and of molecular construction of bodies.

§ 5. These data will be furnished by liquids rather than by solids, because no two specimens of the same solid substance are physically identical. It would be difficult, perhaps impossible, to point to a single solid the material of which has not, at some time or other, been in the liquid or gaseous state. Now, in the overwhelming majority of instances, the parts of the body, at the moment of solidification, arrange themselves in some definite form, either as the rectilinear crystals of definite chemical proportion, or as those more complex forms wrought together by living beings. And it is owing to the varying conditions under which such solidification takes place, that the structure of different specimens of solid matter bearing the same name is so various.

§ 6. Rate of solidification as affected by temperature and pressure, and the presence of foreign bodies which may subsequently be entirely withdrawn, are instances in point in "dead" matter; while the structures of plants and animals are so inconstant that every two specimens of the same organized body differ appreciably from one another even in texture. No solid substances are homogeneous. Metals all show irregular crystallization. The hardest gems have cavities. There are interstices between parts of a crystal which are in optical contact. In short, no sooner does a gas or liquid assume the solid form than it ceases to be homogeneous.

§ 7. But under like external circumstances, two equal volumes of the same liquid are identical. No examination can distinguish the one from the other. The only appreciable difference, the only individuality is that of place.

§ 8. One of the chief difficulties to be overcome in studying the thermal resistances of liquids meets us on the threshold, and arises from the expansion of liquids by heat. If the bottom, sides, or interior of a liquid mass be heated, the whole liquid is gradually set in motion owing to the expansion of the heated portions; and the heat-effects observed at other places in the mass are chiefly due to the convection of heat by the moving liquid.

§ 9. To get rid of such currents two methods are possible, (1) to heat the upper surface of the liquid, (2) to cool the lower one. For by either of these means, the hotter portions of the liquid always rest above the cooler ones, so that no currents can be produced. The two methods should give equally correct and, indeed, in many cases, identical results; in all cases results easily comparable. The choice is a matter of convenience. I have preferred the first, because it is more easy to control exact and constant temperatures of any considerable range when above, than when below the atmospheric temperature.

§ 10. It is clear that when a mass of liquid contained in a vessel is heated from above, the heat will be communicated to the containing vessel. If the latter conduct heat better than the liquid, heat will travel down it more rapidly than down the liquid, and the result will be the establishment of currents such as are shown in Plate LXV. fig. 1 a. If the vessel be a worse conductor than the liquid, it will withdraw from the liquid in contact with it a portion of the heat which has been conducted from above; so that again currents will be established as in Plate LXV. fig. 1 b. In both cases, therefore, the apparent conduction of the heat by the liquid will be modified by the different conducting-power of the vessel. But as the mass of the liquid varies as the cube, while the surface of the vessel varies only as the square of the linear dimension, the disturbing influence of the vessel's walls may be diminished to any amount by increasing its size. Vessels of great size can, however, only be employed for a few liquids.

## II. *Sketch of former Experiments.*

§ 11. The experiments which have been hitherto performed on the conduction of heat through liquids are briefly the following:—

§ 12. Count RUMFORD[*] froze some water at the bottom of a cylindrical vessel. Upon this he poured a known quantity of warm water. After a time the liquid contents of the vessel were again determined, and the increase was found to be so small that it was concluded to arise wholly from the direct contact of the ice with the warm water in the first instance. Count RUMFORD also took two cylinder glasses containing ice frozen to the bottom. Into one he poured boiling water, and into the other an equal weight of water at 0° C. In both cases the ice soon became covered with a layer of water at its maximum density (4° C.). After a time the ice was removed from both vessels and weighed. From the result the experimenter concluded that the quantity melted was nearly the same, and that consequently the water did not conduct the heat.

§ 13. Dr. TH. THOMSON[†] gently heated from below a column of coloured water covered with a column of colourless water, and found that the heat ascended even when no coloration of the upper water-layer took place, and when therefore no sensible diffusion or convection occurred. Such an experiment must be unsatisfactory for reasons already mentioned, unless indeed the water have the initial temperature of between 0° and 4° C., and the lower portion be heated to not above 4° C. In this case only can the water possibly remain in equilibrium, the denser layers being then the lower ones.

§ 14. Mr. J. MURRAY[‡] employed a hollow cylinder of ice as the vessel to contain the liquid under examination. In such a cylinder he placed successively mercury and oil at 0° C. The upper surface of the liquid was heated by means of a vessel of water at 100° C., supported in some cases a little above the liquid, in others in actual contact with it. The object of the ice-cylinder was to get rid of conduction, because the ice on receiving heat does not become warmer,—it melts. But, as pointed out by M. DESPRETZ, the existence of the melted ice and the partial destruction of the vessel complicate and in a great measure invalidate the results. Indeed, in some respects, ice is the worst substance which could be chosen, on account of the distortion of the results due to the great latent heat of water and the small specific heats of mercury and oil. But although quantitative results were out of the question, Mr. MURRAY succeeded in establishing the fact, which we shall find confirmed, that mercury is a better conductor of heat than oil.

§ 15. The question was in this unsatisfactory state when M. DESPRETZ published his first memoir[§] on the subject. M. DESPRETZ filled with water a wooden cylinder painted internally 1 metre high and from 0·218 to 0·405 metre internal diameter, the thickness of the sides being 28 millimetres. At equal intervals down the axis of the cylinder were the bulbs of horizontal thermometers whose stems pierced the side of the cylinder. The column of water was heated from above by means of a copper vessel, the bottom of which was in contact with the upper surface of the column. Into this vessel fresh portions of hot water were poured at intervals of from four to five minutes. After

* RUMFORD, Essays, vol. ii. p. 199.

† NICHOLSON's Journal, vol. i. p. 81.

‡ Arch. vol. xlii. p. 195 ; also GEHLER's Wörterbuch, Art. Wärme.

§ DESPRETZ, Ann. de Chim. et de Phys. 1839, p. 206. Also Comptes Rendus, 1852, p. 540.

between thirty and sixty hours the thermometers became stationary, and from the degrees of heat which they marked, the experimenter concluded that the temperatures (above the air) were in geometrical progression (the intervals being equal), and that accordingly the law of conduction for water is the same as that for solids.   M. DESPRETZ found that the conductivity of salt water is sensibly the same as that of fresh.   Measured in this way, it appeared that water had a conductivity about $\frac{1}{100}$ that of copper.

§ 16.  It was found in these experiments that the axis of the cylinder was hotter than the parts towards the circumference, and that the interior of the wall of the wooden cylinder was cooler than the surface in contact with the liquid.   These circumstances appear to detract somewhat from the value of M. DESPRETZ's results, because the exist-ence of inequality of temperature invariably points to the existence of vertical currents. Granted that the wood conducts worse than the water, what is the consequence ?   Not that the wood is of no influence, for a portion of the heat of the water must necessarily be given to the wall which it touches, albeit more may be given to the water below, so that currents arise according to § 10, Plate LXV. fig. 1 *b*.

§ 17.  Another source of error, as it appears to me, in these experiments, lies in the intermittent manner in which the hot water is renewed in the source of heat.   The time required to produce a given effect must certainly be thereby very materially increased. For when a quantity of hot water is poured in and allowed to stand, not only is the top of the conducting column heated but the bottom of the heating mass is cooled, the two quickly assume nearly the same temperature, which is below that of the water originally added.   When, therefore, a fresh supply of hot water arrives, its heat has to traverse a series of strata of water, each of which is at a lower temperature than it would have been if the supply of hot water had been continuous,—that is, if the upper layer of the column had been maintained at a maximum temperature instead of being only moment-arily raised to that temperature by each successive addition of hot water to the upper vessel.

§ 18.  It seems, indeed, clear that the condition of M. DESPRETZ's column, after the thermometers have become stationary, results from the establishment of thermal equili-brium between the continual accession of heat from above downwards, and the escape of that heat through the sides of the containing vessel by radiation and atmospheric conduction; otherwise it is impossible, with our present knowledge of the nature of heat, to explain the fact observed, that even after sixty hours the lowest thermometers show no increase of temperature in the lower strata of the column.

### III.  *Description and use of the Diathermometer.*

§ 19.  The object immediately proposed in the following investigation was to deter-mine the relative and absolute thermal resistance offered by a given thickness of a given liquid in a given time, when the liquid has a given temperature, and when the tempe-rature difference between the liquid and the source of heat is known.   To effect this, an apparatus had to be devised which would be applicable to many different liquids, and

to solids, and which would be as free as possible from the disturbing influences already pointed out.

§ 20. The extreme sensitiveness of the thermo-electric pile cannot be made use of directly in experiments of this nature. The pile leaves little to be desired where momentary effects of radiant heat are concerned; but it is obviously inapplicable where the quantity of heat has to be considered, as must be the case wherever time is an element of the result.

§ 21. After many trials I have adopted, for the present, the form of instrument described below, and which I believe will be found to answer for a great variety of conditions. The instrument may be called a " Diathermometer." Although it has been hitherto employed exclusively for liquids, it is equally applicable to solids. The apparatus has been skilfully constructed by Mr. W. LADD, of Beak Street, London. The experiments were made partly in the theatre of the London Institution, and partly in the cellar-passage beneath it. Two conditions essential to satisfactory results, are freedom from vibration and uniformity of atmospheric temperature—conditions difficult to obtain in our metropolis and climate, but which were, I think, as nearly as possible satisfied by the solid foundation of the building and the large volume of still air, in or beneath which the experiments were performed.

§ 22. Plate LXV. fig. 2, shows the diathermometer in almost actual size in elevation. Plate LXV. fig. 3 is a view of the entire arrangement of the apparatus. The whole of the diathermometer is of brass, with the exception of the bases of the cones to be described immediately. Upon a mahogany slab, U (fig. 2), there rests a tripod stand, S, supported on two screws, T, T, and the point N. From one end of the stand above N there is fixed the triangular vertical prism M, which terminates above in a very accurately cut screw, K K. Exactly fitting M is a sliding collar, H, to which is screwed the bracket G. The arm F is screwed firmly upon G. One end of F is pierced so as to allow the screw K K to pass through and is clasped by the nut I J, which works accurately upon the screw K K. The head of the nut I, where it is in contact with the arm F, is graduated into 10ths and 100ths. Upon the arm F, beneath the graduation of the nut, is an arbitrary mark, R. The other extremity of F carries a collar, into which is screwed the brass cone A, also provided with a collar, W. The cone A is made of sheet brass, and has the size and shape shown in the figure. Its lower or flat surface is covered with a thin sheet of platinum, which is soldered to the brass. The diameter of the platinum base is 53·34 millims. The neck of the conical flask (A) is provided with a cork (E), through which pass two glass tubes, C and D. The tube C reaches to 0·5 millim. from the bottom of the cone. The tube D is open immediately beneath the cork. Exactly facing A is a perfectly similar cone, B, which is screwed into the centre of the tripod stand, S. The lower cone is also faced with platinum. The neck of B is furnished with a cork, P, through which passes the vertical tube Q, open at both ends. This portion of the apparatus must be scrupulously air-tight. The lower end of Q dips into a wide vessel of coloured water, and carries a paper scale divided arbitrarily, but into exactly equal divisions.

The lower cone and tube form in fact an air-thermometer, the liquid in the stem of which may be adjusted to any height.

§ 23. The platinum surfaces of the cone bases are ground optically flat and polished*. When breathed upon and brought into contact, they fit one another so exactly that the one may be almost lifted by the other, owing to their adhesion. Before being used, they are washed in succession with hot caustic soda, nitric acid, alcohol, and water.

§ 24. It is clear that if the micrometer-screw is read when the cones are in actual contact, and again when they have been removed to some considerable distance (say 10 millims.), we know how much the screw must be turned to give a motion of 1 millim. In my apparatus 1·06 turn of the screw corresponds to 1 millim., and as the screw-head is divided into 100 parts, it is easy to adjust the distance of the platinum faces from one another to 0·005 millim. The platinum faces are brought into an exactly horizontal position by placing a spirit-level on the lower one, and adjusting by means of the screws T, T. A thick ring of vulcanized caoutchouc (X) presses the tripod stand to the board.

§ 25. The upper cone is then brought down to the required distance from the lower one, and the flat cylindrical interval between the two is filled by means of a pipette with the liquid through which the heat has to pass. When the distance ($\delta$) between the faces is small (say 0·5 millim. to 1 millim.), the edge of the liquid is sensibly vertical, and the eye judges very accurately whether the interval is underfilled or overfilled. But at greater distances (from 2 millims. to 12 millims.) the lower portion of the liquid disk bulges out in consequence of the weight of the liquid, although both upper and lower face remain perfectly wetted. Thus at a distance of 6·6 millims., water shows an appearance as in fig. 4, Plate LXV. The mere filling of the interval as full as it will hold is then a very imperfect guide. In such cases small strangulated pipettes are used (fig. 5, Plate LXV.), which deliver a volume of liquid exactly equal to the volume of the interval when the faces are 0·5 millim. or 1·0 millim. apart. By this means, although the edge of the liquid be curved, we at all events know that the volume of the liquid is the same as if it were vertical and straight†.

§ 26. Let us imagine that a known thickness of liquid is between the cones, that the capacity of B is known, that the tube Q has been calibrated, that the temperature of the air has been ascertained, that the height of the liquid in Q is noted, that the barometric pressure has been observed, and that the height of the column of water above the surface in the reservoir has been also measured. If now a current of hot water of known temperature is led through the tube C, the lower surface of A at once assumes and is continually maintained at a known temperature. The heat gradually

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* Held obliquely, the image of a straight line seen on the base of the cone coincides with a straight edge, however the cone may be turned on its axis.

† It is noteworthy how remarkably the cohesive preeminence of water appears in these experiments. Other liquids can be obtained in disks of 4 millims. to 5 millims. only with great care : water may be got in disks of 8 millims., or even 12 millims. It will be remembered that I have elsewhere shown that of all liquids water has the greatest drop-size (Proceedings, Royal Society, 1864). This fact is also to be attributed to the superiority of that liquid in cohesion.

travels downward through the liquid L, warms the platinum face of B, expands the air in B, and depresses the water in Q.

§ 27. The arrangement for leading a current of water of constant temperature through A is shown in fig. 3, Plate LXV. A tinned iron cylindrical vessel containing the water, 1, about 1 metre high and 30 centims. diameter, is heated by a gas-lamp, 2. The gas supplying the lamp passes through the thermostat, 3. Supported near the bottom of the cylinder is a perforated conical mixer, 4*. In the immediate neighbourhood of the bulb of the thermostat is the bulb of the standard thermometer, 5, a small suspended beaker glass, 6, and the shorter limb of the siphon tube, 7. The longer limb 8 of the siphon may be introduced into the funnel 9 connected with the tube C of the diathermometer. The diathermometer itself, 10, is firmly clamped upon a substantial three-legged camera-stand, 11, and a wooden screen, 12, is placed between the lamp and cylinder, 2 and 1, and the diathermometer. A tube attached to the tube D of the diathermometer conveys away the warm water which has passed through the cone A. When one experiment has been made and the instrument has been readjusted by passing cold water through A, the cone A is emptied by forcing air through D; by this means there always remains a film of water on the bottom of A of about 0·5 millim. in thickness.

§ 28. Let us suppose that an experiment has to be made, that the diathermometer has been adjusted, and that the temperature in 1 is the required temperature. The siphon 7, 8 is hung away from the diathermometer and the water is set running through it. About 5ˢ before the appointed time, the beaker, 6, full of warm water is brought to the edge of the funnel, 9. At the appointed time it is emptied into the funnel, into which is immediately placed the end of the siphon, 8. A continual flow of hot water takes place through the cone A, the base of which is therefore thenceforth maintained at a temperature a given number of degrees above the temperature of the air, that is, above the temperature of the liquid, L.

§ 29. The thermometer used was a standard Kew thermometer, the error of which was determined. The readings subsequently given are all reduced to Centigrade.

### IV. *Sources of Error and Corrections.*

§ 30. It is clear that when the hot water passes through the siphon, 7, 8, into the cone A, the water in A is somewhat cooler than in 1, in consequence of the radiation from the siphon and cone and of the atmospheric convection. It is necessary therefore to estimate this loss of heat in order to know at what temperature the water in 1 must be kept, so that the water in A may have the required temperature.

§ 31. The temperature of the air, T, being 18°·16 C., it was found that,

| | | |
|---|---|---|
| When the temperature in 1 was . . . . . 28·16 | 38·16 | 48·16 |
| Then „ „ A „ . . . . 27·88 | 37·51 | 46·40 |
| Loss . . . . 0·28 | 0·65 | 1·76 |

* For description of thermostat and mixer, see Phil. Mag., July 1868.

Thus, in order to get in A a temperature 10° above the atmospheric temperature, T, the water in 1 must be heated to $T+10\cdot28$. To get an excess of 20° in A, the water in 1 must be heated to $T+20\cdot65$, and so on. From these three values, which include almost the entire range of temperatures which I have employed, the intermediate values can be interpolated when required. These values may vary slightly with the atmospheric temperature at the time, but such variation is within the limits of observational error*.

§ 32. *Radiation.*—The question is a vital one, whether, and if so, what proportion of the effect produced in the lower cone is due to radiation through the liquid. If radiation takes place in such a manner as to completely penetrate the liquid and reach the lower platinum surface, the effect would inextricably complicate the phenomena; for while some of such radiant heat would be reechoed upwards and downwards between the cones, a portion would be absorbed by the lower plate, and this would not only augment the expansion of the air in the lower cone, but being shared by the lower part of the liquid (L) in contact with it, currents would be formed and the results vitiated. Such effect might indeed be to a great degree diminished by making the face of the lower cone of fluor-spar or even of glass. But the great thermal resistances of such substances, compared with that of a metal, would more than counterbalance the possible benefit to be derived from their greater diathermancy.

§ 33. Actual experiment, however, showed that the effect of radiation was inappreciably small.

§ 34. It will be admitted that radiant heat would pass with a velocity so great that the time-lapse between its emission from the upper plate and its effect upon the lower cone would be inappreciably small. The following results with water show that, under the following conditions, the time-lapse between the influx of water into A and the commencement of the depression in Q was pretty constant and considerable.

$$T=\text{Temperature of air or initial temperature of liquid}=21°\cdot39$$
$$T_1=\text{Temperature of water in A . . . . . . . .}=31°\cdot39$$
$$\Delta T=\text{Temperature-difference . . . . . . . . .}=10°\cdot00$$
$t=$ Time required to produce first effect in Q.
$\delta=$ Thickness of liquid, L.

|  | $\delta=2$ millims. | $\delta=3$ millims. |
|---|---|---|
| (1) | $t=6$ | $t=10$ |
| (2) | $t=7$ | $t=10$ |
| (3) | $t=7$ | $t=11$ |
| (4) | $t=5$ | $t=11$ |
| (5) | $t=7$ | $t=10$ |
| Mean | $t=6\cdot4$ | $t=10\cdot4$ |

* Strictly the temperatures in 1 should be observed when the temperature in A is fixed; the difference between the results so obtained and those given is vanishingly small.

At greater distances, as we shall see, $t$ may be as much as $20^s$. This time-lapse cannot be due to the obstruction caused by the metal bases; for, as hereafter shown, when nothing intervenes between them, that is, when they are in actual contact, the lapse of time between the influx of hot water into A and the depression in Q is immeasurably small. Even when $\delta = 1$ millim. the time-interval $t$ is sensible.

§ 35. These experiments alone might be considered sufficient to show that at these intervals, at all events, and with water the effect of radiation is practically nothing. The question, however, is so fundamentally important to the investigation that it was examined in another way. The experiment was made as before, with water between the plates, then a disk of Swedish filtering-paper exactly of the same size as the platinum faces was introduced, and the experiment was repeated. In these experiments not only was the time-lapse required for the first effect noted, but the total depression in Q after 1, 2, and 3 seconds was observed. Let these depressions, measured in millimetres, be $\Delta H_1$, $\Delta H_2$, $\Delta H_3$ respectively. We need not reduce these linear depressions to thermal units to recognize the smallness of the effect produced by the interposition of the paper.

$$T = 21°{\cdot}22$$
$$T_1 = 31°{\cdot}22$$
$$\Delta T = 10°{\cdot}00$$
$$\delta = 3 \text{ millims.}$$

|  | $t.$<br>s | $\Delta H_1.$<br>millims. | $\Delta H_2.$<br>millims. | $\Delta H_3.$<br>millims. |
|---|---|---|---|---|
| Water without | 10 | 47·77 | 77·21 | 90·52 |
| paper disk. | 10 | 48·26 | 79·62 | 91·00 |
| Mean | 10 | 48·01 | 78·41 | 90·76 |
|  | s | millims. | millims. | millims. |
| Water with | 10 | 46·81 | 77·21 | 88·59 |
| paper disk. | 10 | 47·27 | 75·76 | 86·67 |
| Mean | 10 | 47·04 | 76·48 | 87·63 |

If we take into account the great thermal resistance of paper, and further, that the absolute bulk of the matter through which the heat has to pass is increased by the introduction of the paper, we are again led to the conclusion that the effect of radiation is negligible.

§ 36. In a previous experiment with another set of cones having brass faces, similar results were obtained. The distance between the cones was about 2·1 millims., but it was not exactly measured; neither was the temperature of the air nor the time-lapse $t$. The depression is given up to the end of 10 minutes.

$$T_1 = 23°{\cdot}06$$
$$\Delta T = 14° \text{ } circa.$$
$$\delta = 2{\cdot}1 \text{ millims. } circa.$$

|  | Water alone. millims. | Water with paper disk. millims. |
|---|---|---|
| $\Delta H_1$ | 113·41 | 108·58 |
| $\Delta H_2$ | 203·61 | 203·61 |
| $\Delta H_3$ | 243·71 | 243·71 |
| $\Delta H_4$ | 267·84 | 262·91 |
| $\Delta H_5$ | 282·34 | 277·39 |
| $\Delta H_6$ | 291·97 | 287·04 |
| $\Delta H_7$ | 301·62 | 296·69 |
| $\Delta H_8$ | 308·76 | 304·04 |
| $\Delta H_9$ | 313·69 | 311·18 |
| $\Delta H_{10}$ | 316·10 | 316·10 |

The absolute coincidence of some of these numbers to the second place of decimals arises from the arbitrary divisions on the scale being reduced to millimetres, and is not therefore a measure of the strictness of the accord. Nor can these results be compared with those of § 34 for the reasons given ; but they bear strong independent testimony to the absence of sensible radiation.

§ 37. As, however, Dr. TYNDALL has deduced from his experiments on radiant heat that water (or at all events a saturated solution of chloride of sodium) is of all transparent liquids examined the most athermanous, it was considered advisable to examine one or two other liquids. On examining amylic alcohol and oil of turpentine in this manner, the depression in Q, when the liquids were alone, was found to be even more strictly equal to that produced in the presence of a paper disk than was shown by water.

The most recent researches of Herr MAGNUS * entirely confirm these results. This experimenter has shown that a certain proportion of non-luminous heat-rays which radiate at an angle of 35° from the surfaces of solids and liquids heated to 100° C. undergo polarization, and that consequently a certain proportion of the heat radiated in this way emerges from beneath the geometrical surface of the body. It would result from this conclusion that all the substances examined are, up to a certain thickness, diathermanous. Such superficial diathermancy is quite consistent with the perfect athermancy of the same substances when employed in sheets or films of the utmost attainable tenuity.

§ 38. The same experimenter has, indeed, shown that when a liquid is raised throughout to 100° by maintaining its lower portion at that temperature, precisely the same phenomena of radiation and polarization of the heat are observed, whether the bottom of the vessel containing the liquid be brightly polished or covered with lampblack. It results from these experiments that the liquids examined, namely rape-oil, resin, wax, glycerine, paraffin, in layers less than 1 centimetre† in thickness, are perfectly athermanous to

* Monatsbericht der Königlich preussischen Akademie der Wissenschaften zu Berlin, April 1868, p. 249.

† The liquid was contained in a metallic dish 1 centimetre deep ; the exact thickness of the liquid layer is not stated.

heat of 100° C. Now if 10 millims. of a liquid are athermanous to a heat-difference of, say, 80°, may not 3 millims. well be athermanous to a heat-difference of 10°?

§ 39. *Diffusion.*—It is well known that when two unequally heated portions of the same liquid, or of two miscible ones are mixed, a state of thermal equilibrium between the two is established, and a temperature results intermediate between those of the mixed liquids, and dependent upon their temperatures, masses, and capacities for heat. If such experiments stood alone, it would be difficult, either by the dynamic or the conditional theory of heat, to disprove the assertion that no interchange of heat takes place between particle and particle,—that each particle maintains its original temperature, and that, being mutually diluted, the effect (for instance on the mercury of a thermometer) is the resultant of two unequal but continual efforts.

§ 40. But the fact that substances in contact establish thermal equilibrium without mutual interpenetration, shows that the first method of heat equalization may and does take place. The question, however, still remains:—Is the equalization of temperature instantaneous when two liquids of unequal temperature are perfectly mixed? When a vessel of cold water is placed over a flame, may not the water at the bottom which has the temperature of the bottom, diffuse into the colder water without immediately losing its temperature*? All analogy, indeed, indicates the high improbability of such an occurrence, but by no means its impossibility. The question is of importance in our present direction of research; for it may be maintained that the heat which appears at the lower cone has been conveyed downwards by the downward diffusion of the warmer liquid at the top, instigated by the difference in density of the upper and lower portions.

§ 41. To set this question at rest, the bottom of the upper cone was painted with a soluble aniline dye. Sufficient water was placed upon the lower cone to fill an interval of 3 millims., and the upper cone was brought down to that distance. The conditions of the experiment were as follows:—

$$T = 13°\cdot3 \text{ C.}$$
$$T_1 = 23°\cdot3 \text{ C.}$$
$$\Delta T = 10° \text{ C.}$$
$$t_1 = 10 \text{ min. } (t_1 \text{ is the duration of the experiment})$$
$$t = 10 \text{ sec.}$$

At the end of 10 minutes, when nearly the maximum depression had been effected, some of the liquid in contact with the lower cone was cautiously withdrawn by means of a capillary pipette. The perfect colourlessness of this portion showed that no convection due to diffusion had taken place; the only other alternative being the diffusion of the water away from the colouring-matter,—a hypothesis sufficiently improbable for us to conclude that no diffusion of the kind occurs.

§ 42. This experiment at the same time furnishes an excellent test of the trust-

* A similar suggestion in regard to air, occurs in MAURY's ' Physical Geography of the Sea ; ' the occasion being the calm-belts of Cancer and Capricorn.

worthiness of the instrument, for it shows the absence of convection from whatever cause.

### V. *Measurement of the Velocity of Heat-penetration, t.*

§ 43. The question as to the rate at which heat passes through liquids immediately involves another, namely :—Does the effect of a greater heat-difference travel faster than that of a less heat-difference? This interesting question may be easily and satisfactorily answered by ₁means of the diathermometer. The conditions of an experiment were (with water):—

$$T = 21°·39$$
$$\delta = 3 \text{ millims.}$$

| | $t.$ | | | | | Mean. |
|---|---|---|---|---|---|---|
| $\Delta T.$ | (1) | (2) | (3) | (4) | (5) | $t.$ |
| $\overset{\circ}{30}·83$ | s 7 | s 7 | s 7 | s 6 | s 7 | s 6·8 |
| 25·83 | 8 | 7 | 8 | 8 | 7 | 7·6 |
| 20·83 | 8 | 8 | 8 | 8 | 8 | 8·0 |
| 15·83 | 9 | 9 | 9 | — | — | 9·0 |
| 10·83 | 10 | 10 | 10 | — | — | 10·0 |
| 5·83 | 12 | 10 | 11 | 11 | — | 11·0 |

It appears distinctly from this Table that when the temperature-difference is greater a more rapid passage of the heat is effected, at all events when the same initial temperature T is taken. There still remains, however, a possibility that the effect may be due as much to the difference of the *quality* of the heat at the higher limit as to the extent of the range. Perhaps there may be no simpler exact means of clearing up this point than the performance of similar experiments, at times when the atmospheric temperature has greatly altered. We shall return to this point in considering the quantity of heat which traverses the liquid disk.

§ 44. When the temperature-difference is small the commencement of the effect is not well marked; hence the tendency of the observer is to overestimate the time; this error is diminished by using a very narrow tube for Q.

§ 45. Sperm-oil and glycerine were examined under the following conditions:—

$$T = \overset{\circ}{26}·5$$
$$T_1 = 36·5$$
$$\Delta T = 10·0$$
$$\delta = 3 \text{ millims.}$$

| | $t.$ | | | Mean. $t.$ |
|---|---|---|---|---|
| | s | s | s | s |
| Sperm-oil . . . . | 17 | 17 | 16 | 16·6 |
| Glycerine . . . . | 11 | 11 | 11 | 11 |

We shall find subsequently that the resistances of the three liquids, water, glycerine,

and sperm-oil (as measured by the number of units of heat equal thicknesses of them arrest in a given time), are in the order just written, the resistance of water being least. I have not at present sufficient data for establishing the relation between the time $t$ and the resistance.

§ 46. If we had found that the time $t$ required for penetration had been the same for heat of all temperatures, we should of course expect to find the time $t$ proportional to the thickness $\delta$. That this is not the case appears from the following experiment with water. The interval between the plates was raised successively from 1 millim. to 6 millims. by degrees of 0·5 millim.; at each half millimetre the time $t$ was measured under preeisely similar circumstances.

$$T = 26\overset{\circ}{\cdot}5$$
$$T_1 = 36\cdot5$$
$$\Delta T = 10$$

| $\delta$. millims. | $t.$ s | s | s | s | s | Mean. $t.$ s | $\Delta t.$ s |
|---|---|---|---|---|---|---|---|
| 1 | 4 | 3 | 3 | 4 | 3 | 3·4 | 1·2 |
| 1·5 | 5 | 4 | 5 | 5 | 4 | 4·6 | 1·8 |
| 2 | 6 | 7 | 7 | 5 | 7 | 6·4 | 2·0 |
| 2·5 | 8 | 9 | 8 | 9 | 8 | 8·4 | 2·0 |
| 3 | 10 | 10 | 11 | 11 | 10 | 10·4 | 2·8 |
| 3·5 | 13 | 14 | 13 | 13 | 13 | 13·2 | 2·2 |
| 4 | 15 | 16 | 16 | 16 | 15 | 15·4 | 3·0 |
| 4·5 | 18 | 19 | 19 | 18 | 18 | 18·4 | 3·6 |
| 5 | 20 | 21 | 21 | 21 | 22 | 21·0 | 2·8 |
| 5·5 | 24 | 24 | 24 | 24 | 23 | 23·8 | 3·2 |
| 6 | 25 (?) | 26 | 27 | 28 | 27 | 27·0 | |

§ 47. It hence appears that the thickness and time of penetration are not directly proportional to one another, but that if one disk of water be twice as thick as another, the thicker one will delay the heat more than twice as long as the thinner one. And this fact may well arise from the one previously established, that heat of a high temperature penetrates more quickly than heat of a lower temperature. For if we imagine two simultaneous experiments in which the heat reaches the middle of the thicker layer exactly at the moment when it has just completely penetrated the thinner one, then the second half of the thicker liquid will have to resist the passage of heat from a source of lower temperature, and this, as we have seen, implies a slower passage. Neither the case where the liquid is very thin, nor that in which it is very thick, is the most favourable for determining the time $t$. In the first the margin of unavoidable error forms a large fraction of the observed time $t$; in the second the commencement of the motion in Q is so gradual that some little time may elapse before it is recognized. The instant of the commencement of a slow motion cannot be so accurately determined as that of a

quick one.   In fig. 6 the points of the curve 1 represent the variation of $t$ with $\Delta T$; those of 2 represent the variation of $t$ with $\delta$.

## VI. *The Quantity of Heat conducted, or Measure of Resistance.*

§ 48.  In order, by means of the expansion of the air in B, to measure the quantity of heat which passes through a liquid under given conditions, or to measure the resistance which the liquid offers to the passage of heat, it is necessary to know the capacity of the lower cone B, and the calibre of the different portions of the tube Q, together with the whole pressure on the air in B.   A Table was formed, which being arbitrary need not be here given, showing the capacity in cubic centimetres of the different parts of Q, which was slightly conical.   The lower cone B and a small portion of Q, as far as a certain point, had the volume 45 cub. centims.

§ 49.  It is clear that the increase of volume in B does not directly give the quantity of heat which passes through the liquid L, because part of that heat is expended in heating the metal of the lower cone; and moreover the heated air in the lower cone accumulates towards the top of the lower cone, so that although the coefficient of air-expansion is virtually the same at all temperatures, yet there being less temperature-difference between the platinum and the air than would be the case if the air in cone B were continually mixed, the ingress of heat must be smaller and the thermal resistance of the liquid would appear too great.   A certain amount of radiation from the lower cone tends in the same direction, as also does the loss of heat due to its expenditure in penetrating the cone bases.   It would be nearly impossible to estimate and allow for all these errors; but they may be eliminated *en masse*.   For if the cones are in the first instance brought into actual contact, and this expansion in B is measured under given experimental conditions, and if then the expansion is also measured when a liquid is inserted under like conditions, then the difference between the two effects is a true measure of the thermal resistance of the liquid, because the same errors being attached with the same signs to both determinations, do not affect their difference.

§ 50.  The platinum faces of the cones were brought into actual contact by wetting their faces with mercury*.   The quantity of mercury so introduced was immeasurably small, and its presence causes a far less error than would attend the presence of an air-film.   It was found that the value of $t$ in all cases was too small for measurement, indeed the transmission of heat appeared instantaneous; it was certainly less than $0^{s}\cdot5$. In these, as in the previous experiments, I have preferred to give the nearest whole number of seconds rather than to attempt to subdivide a second.   The expansions were measured after 1, 2, and 3 min.   The necessary corrections have been made in these numbers for the varying pressure in B.

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* For a method of wetting platinum and other metals with mercury, see a paper by the author on Drops (Royal Society Proceedings, 1864).   When the cone-faces are wetted with mercury and the one face is slid upon the other, the lower cone may be weighted with from ten to twelve pounds before the two are separated.

$$T = 2\overset{\circ}{1}\cdot 22$$
$$T_1 = 31\cdot 22$$
$$\Delta T = 10$$
$$\delta = 0.$$

$\Delta H$, which has to be found, represents the corrected depression in millimetres.

| t. s | $t_1 = 1$ min. $\Delta H_1$. millims. | $t_1 = 2$ min. $\Delta H_2$. millims. | $t_1 = 3$ min. $\Delta H_3$. millims. |
|---|---|---|---|
| 0 | 111·65 | 119·56 | 123·06 |
| 0 | 103·76 | 119·12 | 123·06 |
| 0 | 106·17 | 118·71 | 122·84 |
| 0 | 105·18 | 118·99 | 123·00 |
| 0 | 106·17 | 119·42 | 123·17 |
| 0 | 105·69 | 119·35 | 123·06 |
| Mean . . | 106·44 | 119·19 | 123·03 |

In another experiment, where $t_1 = 1$ min. throughout, $\Delta T$ was taken as $10°$, $20°$, and $30°$ C. in succession.

$$T = 2\overset{\circ}{0}\cdot 17$$
$$T_1 = 30\cdot 17$$
$$T_2 = 40\cdot 17$$
$$T_3 = 50\cdot 17.$$

| t. s | $t_1 = 1$ min. | | |
|---|---|---|---|
| | $\Delta T = 10°$. millims. | $\Delta T = 20°$. millims. | $\Delta T = 30°$. millims. |
| 0 | 106·17 | 235·47 | 414·48 |
| 0 | 105·86 | 233·83 | 422·49 |
| 0 | 106·17 | 234·29 | 421·24 |
| Mean . . $\Delta H =$ | 106·07 | 234·53 | 419·40 |

We can employ these correctionary data to the numbers subsequently obtained when liquids intervene, without previously reducing the linear depression to cubic proportional expansion.

§ 51. *Relation between resistance and thickness.*—We have already obtained some notion of this relation in examining the time $t$ required for heat to traverse different thicknesses of water. Taking the same liquid, we may now estimate the resistance by finding how much heat passes through in a given time, and therefore how much is arrested. The resistance is considered as the number of heat-units (1 grm. 1° C.) which the liquid arrests in a given time; but for our present purpose we need not make the latter reduction; the corrected linear depression in millimetres will suffice.

$$T = 1\overset{\circ}{9}\cdot 28$$
$$T_1 = 29\cdot 28$$
$$\Delta T = 10 \text{ C.}$$
$$t_1 = 1 \text{ min.}$$

| $\delta$. | Resistance mean of five experiments. millims. | $\Delta R$ millims. |
|---|---|---|
| 2·5 | 63·00 | |
| | | 3·09 |
| 3·0 | 66·09 | |
| | | 5·65 |
| 3·5 | 71·74 | |
| | | 8·42 |
| 4·0 | 80·16 | |
| | | 5·88 |
| 4·5 | 86·04 | |
| | | 6·93 |
| 5·0 | 92·97 | |
| | | 2·25 |
| 5·5 | 95·22 | |
| | | 4·56 |
| 6·0 | 99·78 | |
| | | 3·04 |
| 6·5 | 102·82 | |

It is seen, on comparing the numbers of column $\Delta R$ millims., that there is a continual increase of resistance with the thickness, but it would not be safe from these numbers to attempt to deduce any law (see fig. 6).

§ 52. *Relation of resistance to time $t_1$ and temperature.*—In another series of experiments a set of brass cones were employed having brass bottoms. The depression when they were in contact was not measured. The interval $\delta$ can only be considered approximately as 2 millimetres, but it was perfectly constant throughout. For these reasons the numbers given can only be compared *inter se*. The necessary reductions are made for pressure. The depression produced by the passage of water of a certain temperature through the upper cone was allowed to attain a maximum, and then water of a known higher temperature was passed through. The water in the interstice was brought to a uniform temperature by stirring with a slender wooden splinter. The numbers are given in the units of the arbitrary scale (1 H=4·826 millims.).

$$H=37$$
$$T =13°·06$$
$$\Delta T= 5°·55$$
$$\delta=2 \text{ millims. } circa.$$

| $t_1$. | $T_1-T=5°·55.$ $H_1.$ | $T_2-T_1=5°·55.$ $H_2.$ | $T_3-T_2=5°·55.$ $H_3.$ | $T_4-T_3=5°·55.$ $H_4.$ | $T_5-T_4=5°·55.$ $H_5.$ |
|---|---|---|---|---|---|
| 1 min. | 47 | 71 | 110 | 146 | 180 |
| 2 | 55 | 84·5 | 122 | 156 | 192 |
| 3 | 58 | 89·5 | 128 | 160 | 196 |
| 4 | 59 | 91·0 | 129·5 | 161 | 196 |
| 5 | 60·5 | 91·5 | 130·5 | 161 | 196 |
| 6 | 61 | 92·2 | 131 | | |
| 7 | 61 | 92·5 | 131 | | |
| 8 | . . . . . . . | 92·5 | 131 | | |
| 9 | . . . . . . . | 92·5 | 131 | | |
| 10 | . . . . . . . | 92·6 | | | |

It appears from the above Table that warm water conducts more heat than cooler in the same time for the same temperature-difference. The temperature-difference being constant ($5°55$ C.) the corresponding expansions are in one minute

| from  $T = 13°06$ | from $T_1 = 18°61$ | from $T_2 = 24°16$ | from $T_3 = 29°71$ | from $T_4 = 35°26$ |
|---|---|---|---|---|
| to    $T_1 = 18°61$ | to    $T_2 = 24°16$ | to    $T_3 = 29°71$ | to    $T_4 = 35°26$ | to    $T_5 = 40°81$ |
| Expansion $= 10$. | Expansion $= 10$. | Expansion $= 11·4$. | Expansion $= 15$. | Expansion $= 19$. |

We also conclude from the above deduced values, not only that the resistance diminishes with the temperature, but also that the diminution of resistance is greater for equal increments of temperature at higher than at lower temperatures.

§ 53. The first of these results, namely, that resistance diminishes with increase of temperature, agrees fully with the result given in §§ 43, 46, that the rate of penetration $t$ is less for less temperature-differences than for greater ones. The cause of the more speedy penetration of great heats is in fact due to the less resistance offered to the passage of the heat by those portions of the liquid which have already been heated.

VII. *Influence of Constitution of the Liquid on the quantity of the Heat which passes.*

§ 54. In experimenting in the manner described in §§ 15, 16, M. DESPRETZ concluded that the conductivities of fresh and salt water were virtually the same. The important cosmical bearing of this question induced me to examine it by means of the diathermometer, and at the same time to examine the relative conducting-powers or resistances of some other aqueous solutions. Preliminary experiments having shown that the resistances of such solutions were very nearly the same as that of water, I have preferred for the present the examination of saturated, or nearly saturated solutions to those which contain either equal or equivalent amounts of solid salt. The solutions of the pure salts were saturated at the atmospheric temperature, and a single drop of water was added to each to prevent crystallization during the experiment, which would of course vitiate the result. The results are given, as before, in corrected millimetres of depression; the numbers are in the proportion of the numbers of heat-units arrested (comp. § 50).

$$T = 19°72$$
$$\Delta T = 20$$
$$\delta = 2 \text{ millims.}$$
$$t_1 = 1 \text{ min.}$$

| | millims. | millims. | millims. | Mean resistance. millims. |
|---|---|---|---|---|
| Distilled water . . . . . . | 99·64 | 101·77 | 100·71 | 100·70 |
| Chloride of sodium (nearly sat.) | 101·11 | 101·72 | 101·47 | 101·43 |
| Chloride of calcium (  „    „  ) | 105·68 | 104·43 | 104·96 | 105·02 |
| Carbonate of potassium („   „  ) | 109·20 | 107·13 | 111·47 | 109·26 |

The two latter of these substances were chosen on account of their great solubility.

§ 55. Two aqueous solutions were now taken of salts whose metals in the elementary state have little resistance, namely, silver and copper. These were again compared with water.

$$T = 20\overset{\circ}{\cdot}83$$
$$\Delta T = 20$$
$$\delta = 2 \text{ millims.}$$
$$t_1 = 1 \text{ min.}$$

|  |  | Water. millims. | Nitrate of silver (nearly sat.). millims. | Sulphate of copper (nearly sat.). millims. |
|---|---|---|---|---|
| Resistance | (1) | 98·64 | 106·64 | 104·22 |
| ,, | (2) | 99·60 | 104·23 | 105·72 |
| Mean . . . |  | 99·12 | 105·43 | 104·97 |

The difference between this value for water and the value given in § 54 may partly arise from the difference $(0^{\circ}\!\cdot\!8)$ of T, but is more probably due to a minute error in $\delta$, as the cones had been separated between these two experiments. It is also seen that there are in one or two cases greater differences between the determinations of the same substance than between those of different substances. In order to get results of sufficient accuracy for the establishment of the law of resistance under these circumstances, a very much greater number of experiments must be performed with an instrument of greater sensibility. I hope to be able to lay such results on a future occasion before the Society.

§ 56. Meanwhile the following conclusions appear unavoidable, even from the above incomplete experiments. The solution of a metallic salt in water invariably increases the thermal resistance of the water. Those elements which dissolve in the water without increasing the bulk of the water, can only increase its thermal resistance by increasing its capacity for heat, which must in such cases be the sum of the capacities of the water and elements separately. The thermal resistance of a solid salt is greater than that of water, consequently when, as in the majority of instances, water is displaced by the salt, the increased resistance is due to the partial substitution of a body of greater resistance. This increase is partly counterbalanced by the inferior specific heat of the salt. The nature of the metallic base of the salt in regard to its thermal resistance in the free state has little influence upon the thermal resistance of the solution of the salt*.

§ 57. The difference in thermal resistance between fresh and salt water must be of very considerable importance in thalattology, but the consideration of this would be beyond the scope of my present purpose.

§ 58. A branch of the investigation of surpassing interest is the comparison of the resistances offered by liquids of entirely different chemical composition. In the experiments the results of which are given below, in order that the experiments might be as exact as possible, times were chosen at which the atmospheric temperature was the

* I am inclined to think that it has none. Compare also § 70.

same; several weeks were thus employed.   The cones were not moved during this time, so that even if there was a minute error in the value of $\delta$ ($\delta = 1$ millim.) the results would be at all events comparable.   The column of specific resistances is obtained by dividing the resistances of the other liquids by that of water, which of all transparent liquids appears to have by far the least thermal resistance.

§ 59.   With regard to the purity of the substances, they had in many cases been prepared for research by Mr. CHAPMAN or Mr. WANKLYN (to whom I am indebted for specimens), with special view to their absolute purity.   The glycerine was heated on a water-bath for a day, and kept *in vacuo* over sulphuric acid for several days.   The acetone was prepared by myself from acetate of barium, and had been combined with sulphite of ammonium.   The water was well boiled immediately before use.   The sperm-oil was the ordinary commercial, which had been kept for several hours at 100° C.   The alcohol was dried over carbonate of potassium, and twice distilled from quicklime.   The nitrobenzol was simply dried and distilled; it might from its history contain a little nitrotoluol. The amylic alcohol when dried boiled at 132° C.   The oil of turpentine was commercial, which had been rectified.   The chloroform was also commercial; it was alternately shaken with strong sulphuric acid and sticks of potash.   The remainder, acetic acid, oxalate of ethyl, acetate of ethyl, oxalate of amyl, butylic alcohol, acetate of amyl amylamine, nitrate of butyl, bichloride of carbon, mercury amyl, bromide of ethylen, iodide of amyl, iodide of ethyl, were all either analyzed or titrated by one of the above-named chemists or by myself, and were shown to be of exceptional purity.   The final drying was, wherever possible, performed by means of anhydrous phosphoric acid.

§ 60.   On account of their volatility some of these liquids might be supposed to give resistances too high.   I was, indeed, unable to examine ether and bisulphide of carbon on this account.   But those in the Table were seen to lose an inappreciably small quantity by vaporization, and to produce before being heated scarcely any elevation of the water in Q.   For various reasons, it is probable that the number for iodide of ethyl is wrong, and that this liquid is misplaced.   An idea of the amount of surface exposed may be got by imagining a tube 13·4 millims. long and 1 square millimetre section, closed at one end, filled with the liquid and exposing therefore at the open end 1 square millimetre.

$$T = \overset{\circ}{20}\cdot17 \ C.$$
$$T_1 = 30\cdot17$$
$$\Delta T = 10$$
$$\delta = 1 \ \text{millim.}$$
$$t_1 = 1 \ \text{min.}$$

| | Thermal resistance in millimetres. | Specific Thermal resistance. |
|---|---|---|
| Water . . . . . . . . . | 4·13 | 1·0 |
| Glycerine . . . . . . . | 15·85 | 3·84 |
| Acetic acid (glacial) . . . . | 34·63 | 8·38 |

| | Thermal resistance in millimetres. millims. | Specific Thermal resistance. |
|---|---|---|
| Acetone . . . . . . . . | 35·14 | 8·51 |
| Oxalate of ethyl . . . . . | 36·56 | 8·85 |
| Sperm-oil . . . . . . . | 36·56 | 8·85 |
| Alcohol . . . . . . . . | 37·53 | 9·09 |
| Acetate of ethyl . . . . . | 37·53 | 9·09 |
| Nitrobenzol . . . . . . | 40·81 | 9·86 |
| Oxalate of amyl . . . . . | 41·29 | 10·00 |
| Butylic alcohol . . . . . | 41·29 | 10·00 |
| Acetate of amyl . . . . . | 41·29 | 10·00 |
| Amylamine . . . . . . | 41·88 | 10·14 |
| Amylic alcohol . . . . . | 42·26 | 10·23 |
| Oil of turpentine . . . . . | 48·53 | 11·75 |
| Nitrate of butyl . . . . . | 49·01 | 11·87 |
| Chloroform . . . . . . | 49·98 | 12·10 |
| Bichloride of carbon . . . . | 53·35 | 12·92 |
| Mercury amyl . . . . . . | 53·35 | 12·92 |
| Bromide of ethylen . . . . | 54·34 | 13·16 |
| Iodide of amyl . . . . . | 54·80 | 13·27 |
| Iodide of ethyl . . . . . . | 58·66 (?) | 14·20 (?) |

§ 61. A special determination was made with the strongest oil of vitriol, $H_2SO_4$, and with the same diluted with fourteen times its volume of water. The strong sulphuric acid showed a specific resistance of 1·33, and the dilute of 1 exactly.

§ 62. The results obtained from endeavours to connect mercury with the above series have given me the number 0·13 as the specific resistance of that metal. But there is so little difference between the depression produced when the cones are in contact, and that which occurs when 1 millim. of mercury interposes, that a slight error in observation would make a very great difference. I give this number for mercury therefore with very great reserve, and only to show that the resistance of water is many times greater than that of mercury.

§ 63. At the conclusion of one of his papers " On the Absorption of Heat by Liquids," Dr. TYNDALL uses the expression " bisulphide of carbon is the rock-salt of liquids." It appears from the Table (§ 60) that we may with equal propriety say that "water is the silver of liquids," at least of the non-metallic ones; for it shows as great a preeminence amongst liquids as silver does amongst metals.

§ 64. It appears that after water itself those liquids have least resistance which contain hydrogen easily replaceable by a metal, as acetic acid, sulphuric acid, and gly-cerine. This fact forcibly suggests the experiments of Herr MAGNUS on the conducti-vities of the gases, and the extraordinarily great conductivity of hydrogen. As, however,

the conclusions drawn by Herr MAGNUS from his experiments have been questioned by Dr. TYNDALL and other physicists, I refrain from doing more than point out this distinct coincidence.

§ 65. Of bodies belonging to the same chemical series or isotypic bodies, those have the least thermal resistance which have the simplest constitution. Thus the resistances of the three alcohols examined are in the order amylic, butylic, and ethylic. Again, the acetate of amyl has greater thermal resistance than the acetate of ethyl, and the oxalate of amyl than the oxalate of ethyl. The only exception to this appears to be the iodide of ethyl in comparison with the iodide of amyl; but, as before stated, I am disposed to reject the determination of the former body.

§ 66. The only one of these liquids which contains a metal is mercury amyl, and this was tried under the expectation that, owing to the chemical construction of the body, the metallicity of the mercury in regard to its conductivity might appear. Contrary to anticipation, the liquid has one of the greatest resistances.

§ 67. Another noteworthy circumstance is the great specific resistance of all the liquids which contain halogens. May it be owing to the halogenous function of the mercury in the mercury amyl, which brings that liquid to so low a place?

The existence of these regularities and consistencies supports, at all events, the approximate and relative accuracy of the determinations, and by furnishing a new equation of physical property, opens a wide field for future research.

§ 68. If the results just given concerning thermal resistance be compared with those of Signor MELLONI and Dr. TYNDALL with regard to diathermancy, and especially with those of the latter philosopher concerning the absorption of radiant heat by various liquids, a striking dissimilarity at once appears. Taking the four liquids common to both, water, alcohol, acetate of ethyl, and chloroform, Dr. TYNDALL found that of 100 heat-rays of an Argand burner they absorbed—

|  |  |
|---|---|
| Water (saturated with Na Cl) . . . . . . | 86·1 |
| Alcohol . . . . . . . . . . . . | 78·6 |
| Acetate of ethyl . . . . . . . . . | 74·0 |
| Chloroform . . . . . . . . . . . | 25·0 |

respectively when the thickness was 0·04 inch (1 millim.=0·03937 inch). These liquids are accordingly in exactly the inverse order to that in which they appear in the Table, § 60*. That this apparent contradiction is in fact a coincidence appears from the following considerations.

§ 69. The diathermancy of a liquid towards radiant heat, and its resistance to contact heat, are partly due to one and the same cause. The amount of absorption of radiant heat by a liquid, as determined by Dr. TYNDALL, is estimated by the quantity of heat which passes through the body so as to affect the thermomultiplier; and the amount of absorption is directly proportional to the athermancy. Now a liquid which absorbs

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* To my great regret I have not yet been able to determine the resistance of bisulphide of carbon; but I scarcely hesitate to predict that it has a very great, perhaps the greatest thermal resistance.

heat well, and is consequently highly athermanous, forms on that very account an abundant source of heat to bodies in contact with it. And if the heat move through the liquid, by way of conduction, with facility, the quantity of heat which the heated liquid gives up in a given time to another body in contact with it, is great—that is, the resistance of the liquid is found to be small.

§ 70. Though more or less heat passes instantly through a partly athermanous liquid, yet some is absorbed, and the amount absorbed, and therefore the degree of athermancy, is not independent of the specific heat of the liquid; for the transmitted heat is measured before the liquid has become a secondary source of radiant heat in virtue of the heat which it has arrested. It is found, indeed, that the order of absorption in the case of water, alcohol, and bisulphide of carbon is the same as that of the specific heats of the same liquids.

§ 71. With contact heat the case is different; for when a liquid has a high specific heat, although the rise of temperature will be small when the heat enters it, yet this small increment of temperature corresponds to a large absolute accession of heat; so that when, as in my experiments, the liquid becomes a source of heat the absolute quantity of heat given out is also great; hence the specific heat of the liquid in these contact experiments is of no influence. Accordingly we need not look to the different nature of the heat employed to reconcile my experiments with those of Dr. TYNDALL.

§ 72. Concerning the relation between thermal and electrical resistances, a few remarks may be allowed. It has been shown in §§ 46 *seq.*, §§ 52 *seq.*, that the hotter a liqiud (water) is, the less is its resistance, both as measured by the time $t$ required for the first penetration, and by the quantity of heat arrested in a given time-lapse. This is in accordance with the observations of WIEDEMANN, who found that the resistance of a solution of sulphate of copper diminished more than one half when its temperature was raised 55° C., and with the general law of liquids that the resistance diminishes as the temperature increases. With metals, as has been long known, the electrical resistance increases with the temperature. If, therefore, in the case of electricity the law connecting resistance with temperature is the reverse with liquids to what it is with solids, it may well be so with heat; so that while hot solids may conduct heat worse than cold ones, a hotter liquid may conduct heat better than a colder one.

§ 73. The experiments § 61 were especially made to determine whether the addition of sulphuric acid, which so greatly diminishes the electrical resistance of water, has a similar effect upon its thermal resistance. As with electricity so with heat, we find that strong sulphuric acid has greater resistance than dilute. But in the case of heat we do not find that enormous difference in resistance between water and dilute sulphuric acid which is found with electricity. Nor are we justified in expecting it; for in the case of the electrical resistance of a mixture or compound of electrolytes the magnitude of the effect is measured ultimately by the degree of induced polarity; in the case of thermal resistance, it appears to depend arithmetically upon the quantities and respective resistances of the constituents.

§ 74. In order to calculate the number of heat-units arrested by a mass of liquid of given thickness and surface, we must proceed as follows.   Take, for example, the depression-difference for water, § 60, namely, 4·13 millims.   This has, like all the other values of the resistances, been corrected for the calibre of the tube and for the variation in pressure.   It is found from the Tables that

<div align="center">4·13 millims. is equivalent to 0·02829 cub. centims.,</div>

or

<div align="center">45 cub. centims. have become 45·02829 cub. centims.;</div>

hence from

$$x° \times 45 \times 0·00366 = 0·02829$$

we find

$$x° = 0·17177,$$

that is, an amount of heat has been arrested which would heat

<div align="center">45 cub. centims. of air through 0°·17177 C.,</div>

or

<div align="center">1 cub. centim. of air through 7°·72965 C.,</div>

or

<div align="center">1 cub. centim. of water through 7·72965 × 0·237 × 0·001296,</div>

where 0·237 is the specific heat of air for constant pressure, and 0·001296 is the specific gravity of air (both referred to water).   Consequently the heat arrested would heat 1 cub. centim. of water through 0°·0023732 C.   This number, therefore, expresses the number of heat-units arrested in 1 minute by a circular disk of water 53·34 millims. in diameter and 1 millim. in thickness.   Hence the number of heat-units arrested in 1 minute by a layer of water 1 millim. thick and 1 square decimetre of surface is

<div align="center">0·0106.</div>

Calling $U_r$ the number of heat-units resisted, we thus find:—

| | Number of heat-units arrested in 1 minute by 1 square decimetre, 1 millim. in thickness when T=20°·17 C. and ΔT=10° C. $U_r$. |
|---|---|
| Water | 0·0106 |
| Glycerine | 0·0407 |
| Acetic acid | 0·0888 |
| Acetone | 0·0902 |
| Oxalate of ethyl | 0·0938 |
| Sperm-oil | 0·0938 |
| Alcohol | 0·0963 |
| Acetate of ethyl | 0·0963 |
| Nitrobenzol | 0·1045 |
| Oxalate of amyl | 0·1060 |
| Butylic alcohol | 0·1060 |

Number of heat-units arrested
in 1 minute by 1 square decimetre,
1 millim. in thickness when
T=20°·17 C. and ΔT=10° C.
$U_r.$

| | |
|---|---|
| Acetate of amyl . . . . . . | 0·1060 |
| Amylamine . . . . . . . | 0·1075 |
| Amylic alcohol . . . . . . . | 0·1084 |
| Oil of turpentine . . . . . . | 0·1245 |
| Nitrate of butyl . . . . . . | 0·1258 |
| Chloroform . . . . . . . . | 0·1283 |
| Bichloride of carbon . . . . . | 0·1369 |
| Mercury amyl . . . . . . . | 0·1369 |
| Bromide of ethylen . . . . . | 0·1395 |
| Iodide of amyl . . . . . . . | 0·1407 |
| Iodide of ethyl . . . . . . . | 0·1505 |

In submitting these results to the Royal Society I am fully conscious of their incompleteness. I hope shortly to be able to extend my experiments, and to increase their accuracy. Meanwhile I would invite physicists to this interesting and important field of research, which promises an abundant yield to many independent cultivators.

My thanks are due to the Managers and Professors of the London Institution for affording me an opportunity of carrying out my experiments.
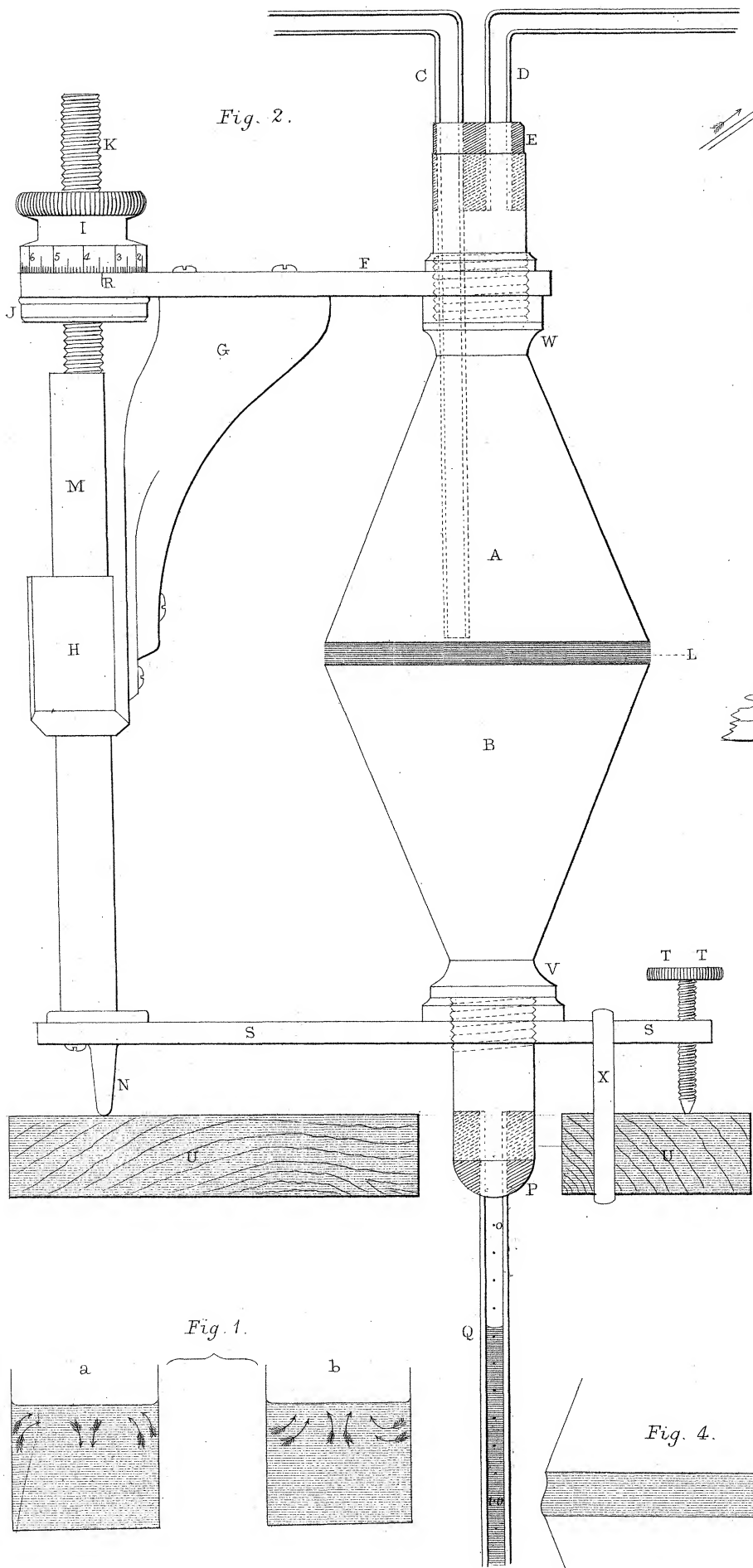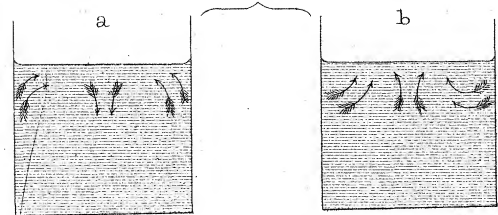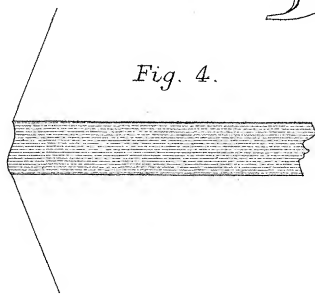
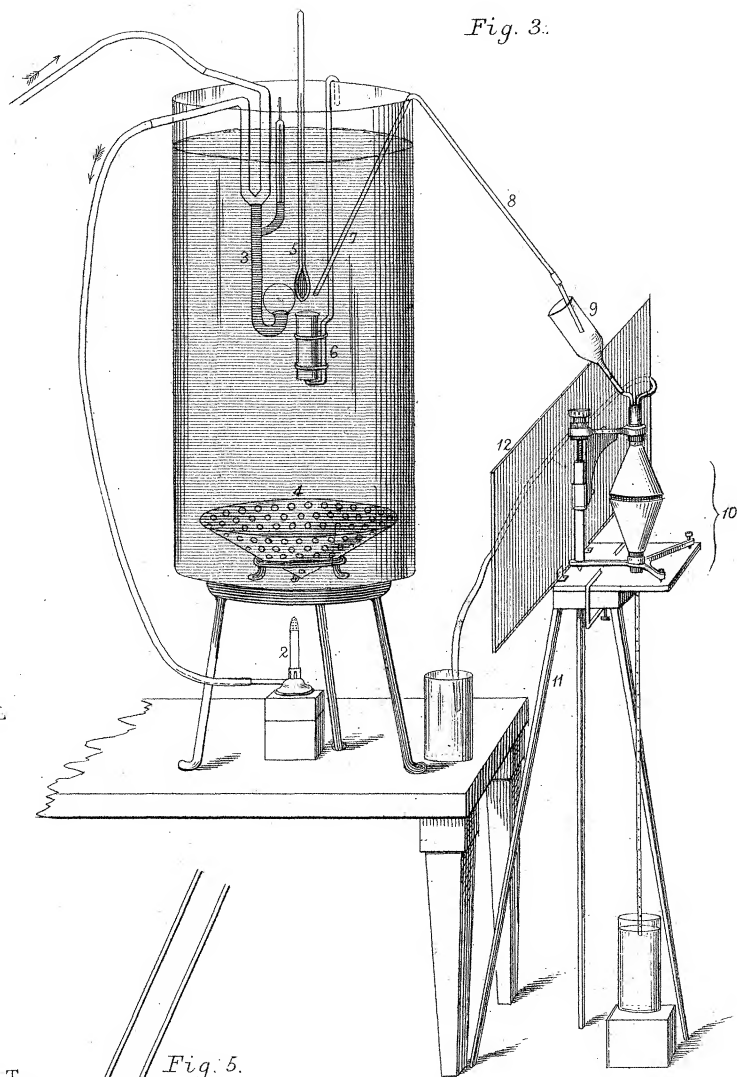Fig. 2.

Fig. 3.

Fig. 5.

Fig. 6.

Fig. 1.

Fig. 4.